CHEMICAL & ENGINEERING NEWS

C&EN

NOVEMBER 1, 1993

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Environmental and economic pressures force changes in papermaking Page 28

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CHEMICAL & ENGINEERING NEWS

C&EN

NOVEMBER 1, 1993

NEWS OF THE WEEK

■ AAAS's Project 2061 releases guidelines for what students should know in science, math, and technology at specific points in primary and secondary school. **Page 4**

■ Third-quarter earnings are up for many major chemical producers, as the earnings turnaround that began in the second quarter continues. **Page 5**

■ American Chemical Society sets ambitious plans for National Chemistry Week, Nov. 7–13, including radio morning talk show appearances by ACS president Helen M. Free. **Page 5**

■ CD26, an enzyme found on surface of immune system cells, appears to act in concert with another cell-surface protein, CD4, to enable AIDS virus to invade the cells. **Page 6**

■ First Technology Reinvestment Project grants were announced last week—a total of $140 million will fund 41 proposals. **Page 7**

■ University of Pennsylvania observes centennial of its chemical engineering program, awards distinguished service medals to three chemical engineers. **Page 7**

COVER: Weyerhaeuser's pulp and paper plant at Columbus, Miss.

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ISSN 0009-2347

BUSINESS

Covenant between Dutch government and chemical industry calls for major cuts in emissions from plants and other steps to improve the environment to be accomplished by 2010. **Page 11**

European chemical market researchers discuss problems, ways to survive in the current depressed economies at their annual meeting in Madrid. **Page 14**

Touting the virtues of the North American Free Trade Agreement and pushing for its passage is the current mission of Dow Mexico president L. Kip Smith. **Page 16**

Ten U.K. fine chemicals companies complete a U.S. promotional tour that is designed to establish supply relationships with U.S. chemical and drug firms. **Page 19**

GOVERNMENT

Chemical industry representatives meet with chemical weapons treaty's Preparatory Committee to establish communication channels concerning the pact's implementation. **Page 21**

Administration testimony on NAFTA to Senate committee paints dire environmental picture if the treaty does not pass. **Page 23**

SCIENCE/TECHNOLOGY

Chemistry pioneer Gilbert Norton Lewis is honored by his hometown and state, 47 years after his death, through determined efforts of local retiree. **Page 25**

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Biography of atomic scientist Leo Szilard pays tribute to the eccentric, iconoclastic genius who conceived the nuclear chain reaction and sought measures to control its use. **Page 42**

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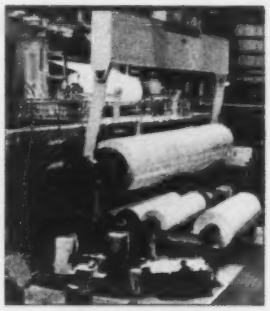

Paper and paperboard comprise a multi-billion-dollar industry that uses vast amounts of natural resources, equipment, energy, and chemicals; but paper chemical suppliers face strong environmental pressures and major changes in their pulp and paper markets. Page 28

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1155—16th St., N.W., Washington, D.C. 20036
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Published by
AMERICAN CHEMICAL SOCIETY
(202) 872-4600; TDD (202) 872-4432
John Kistler Crum, Executive Director
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Subscription Rates 1993: Printed editions: nonmembers U.S. 1 yr. $110, 2 yr. $198; outside U.S. 1 yr. $148, 2 yr. $274. Air freight rates available on request. Rates above do not apply to nonmember subscribers in Japan, who must enter subscription orders with Maruzen Co. Ltd., 3–10 Nihonbashi 2-chome, Chuo-ku, Tokyo 103, Japan. Tel: (03) 272-7211. Single copies: Current $18. Rates for back issues and volumes are available from Microforms & Back Issues Office, ACS, 1155—16th St., N.W., Washington, D.C. 20036. Back and current issues available on microfilm and microfiche. Rates on request from Microform Program, ACS.

Chemical & Engineering News (ISSN 0009-2347) is published weekly except for the last week in December by the American Chemical Society at 1155—16th St., N.W., Washington, D.C. 20036. Second-class postage paid at Washington, D.C., and additional mailing offices. POSTMASTER: Send address changes to Chemical & Engineering News, Membership & Subscription Services, P.O. Box 3337, Columbus, Ohio 43210. ACS assumes no responsibility for the statements and opinions advanced by the contributors to its publications.

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LETTERS

Glycoprotein anchors

One of the Science/Technology Concentrates (C&EN, Aug. 30, page 20) describes the synthesis of the anchor linking Thy-1 to cell surfaces [*J. Am. Chem. Soc.*, **115,** 7886 (1993)]. Two points in this summary require clarification.

First, Thy-1 is a protein with a specific class of glycoprotein anchor—a glycosyl phosphatidylinositol (GPI) anchor. This is not common to all cell-surface glycoproteins. GPI anchors were first described by M. W. Stein and C. F. Logan Jr. [*J. Bacteriol.*, **85,** 369 (1963)], and the first complete structure of a GPI anchor (that of the variant surface glycoprotein of *Trypanosoma brucei*) was elucidated by M. A. J. Ferguson, S. W. Homans, R. A. Dwek, and T. W. Rademacher [*Science*, **239,** 753 (1988)]. GPI anchors contain a tetrasaccharide linked glycosidically to phosphatidylinositol. There may be a variety of substituents on the core polysaccharide structure, and the lipid portions of the anchor are also variable.

Second, Thy-1 may be the most thoroughly studied of the mammalian GPI-anchored proteins, but others include human erythrocyte acetylcholinesterase; placental alkaline phosphatase; and the complement regulatory protein, decay accelerating factor. A review of GPI-anchor biosynthesis in these and other proteins has been recently published by P. T. Englund [*Ann. Rev. Biochem.*, **62,** 121 (1993)].

These small points of elaboration in no way diminish the accomplishments of Bertram O. Fraser-Reid and his colleagues. Access to milligram amounts of this structure can only further knowledge of all the others.

Donna J. Carothers
Cleveland Heights, Ohio

MTBE possibly unsafe, useless

The title of the article "Health Studies Indicate MTBE Is Safe Gasoline Additive" (C&EN, Sept. 20, page 9) is misleading. Information in the article does not support the conclusion stated in the title.

Methyl *tert*-butyl ether (MTBE) is added to gasoline under federal mandate to reduce carbon monoxide levels in automobile exhaust. Your article concluded that it is safe to add MTBE to gasoline, because tests show that most people do not suffer obvious harm from inhaling MTBE vapor. However, you presented no test results that would show that the exhaust fumes from a vehicle operating on oxygenated gasoline are "safe." How can any conclusion be drawn about the safety of a fuel additive, whose purpose is to reduce noxious exhaust emissions, unless the combustion products of the fuel are tested?

An earlier issue (C&EN, April 12, page 28) reported that tests in Colorado have shown that use of the oxygenating additive MTBE does not reduce carbon monoxide levels in the environment and actually increases the levels of other more noxious pollutants containing oxygen, such as aldehydes and ketones. These kinds of compounds can be irritants and can cause cancer and respiratory problems. The use of MTBE caused so many health problems in Fairbanks that its use was discontinued there. These problems were probably caused by the combustion products of the fuel, not the fumes from the fuel tank. However, your article indicated that investigations of the problems focused on fumes from the fuel, not on what is produced in the exhaust. The Environmental Protection Agency doesn't look for carbon monoxide coming out of the gas tank; it measures the carbon monoxide coming from the tailpipe. It is inconceivable that EPA didn't check the vehicle exhaust. Perhaps the results were just not made available to or reported by your staff.

What are the hydrocarbon, nitrogen, sulfur, and oxygen compounds in exhaust from cars burning oxygenated fuels? What environmental levels of these compounds result from the use of oxygenated fuel? Are these safer and less noxious than those from normal gasoline? How much is produced per mile of vehicle use? Does it vary with the age of the vehicle or with ambient conditions (as in Alaska)? Good science would answer questions like this in addition to those relating to MTBE fumes.

Your article didn't mention that oxygenated fuel also causes serious problems with automobiles. Last October, with the first tank of oxygenated fuel, my 1987 Pontiac developed a "bucking" condition. When I asked the dealer for an engine tuneup, he said that the transmission

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Dutch Plan Sets Environmental Targets for Chemical Industry

■ ***Pact between industry and government calls for severe reductions in emissions from plants in three stages by 2010***

Patricia L. Layman, C&EN London

Among their European neighbors, the Dutch are well known to be a people of great tolerance. They are also well known as a people who seek consensus in settling national problems or issues. Their latest such effort at consensus, now under way, directly affects the chemical industry.

The Dutch effort is a "covenant"—established between the nation's government and its chemical industry—to move the Netherlands forward in sustainable development, toward the year 2010, by cutting emissions from chemical production at both large and small chemical companies. The agreement is even accepted, in principle, by many of the country's tough environmental groups, although they have serious reservations on such aspects as timing and extent of the efforts.

At present, about 1700 covenants are in force in the Netherlands, on all sorts of subjects. They are part of the country's culture. Whether the Netherlands' experience could ever yield lessons applicable in more confrontation-oriented countries is debatable, although chemical industry associations in other European countries, and CEFIC, the European Chemical Industry Council, have been discussing the subject with their Dutch counterparts. Meanwhile, the experience is a breath of fresh, rational air in the global environmental debate.

In essence, the covenant the Netherlands government has worked out, in discussion with industry, regional, and local authorities, provides a national plan to tackle environmental problems generated during chemical production processes. The chemical industry's plan, now being implemented, is the third, following those covering the primary metals and printing industries last year.

The chemical industry has committed itself to supporting the national plan, which sets forth firm sectoral goals for 2000 and targets for 2010. The government, in turn, has pledged to not unilaterally change its standards or requirements during this time. The Dutch government thereby achieves its strategic goals of lessened environmental pollution. And the industry's managers can incorporate the goals into their long-term investment planning.

The national plan for the chemical industry was signed in The Hague in April, and the industry was given until September to digest its content and begin working on individual company plans. Each company will write a plan for each plant site, contributing toward reduction of process pollution. Companies have now begun working on these plans, which are scheduled for completion and for presentation to the government in 14 months, according to Willem Quik, technical director at the Association of the Dutch Chemical Industry, VNCI (Vereniging van de Nederlandse Chemische Industrie), in Leidschendam, just outside The Hague.

As VNCI pointed out when the agreement was signed by the parties, to realize the aims of the covenant, the chemical industry will have to invest more than 10 billion guilders—roughly $5.7 billion—from 1993 to 2000. The starting premise was that environmental measures must be technically and economically feasible, as the industry works to meet the industrywide targets set in the national environmental plan. This has led to compilation of an "emissions profile" detailing emissions in the base-year 1985 by the chemical industry.

The chemical industry will gear its policy to implementing the plan in three phases: the first running until 1995; the second, to 2000; and the third, to 2010. All aspects of environmental policy have been included: not only emissions into water, soil, and air, but also energy savings, reduction of process wastes, soil decontamination, external safety, odor and noise nuisance, and internal corporate environmental management systems.

The agreement also provides for

Environmental covenant being signed earlier this year by Ruud Selman, who was president of VNCI at the time, as government and other officials looked on

streamlining and coordinating the activities of the various public authorities. Central government, the provinces, the municipalities, and the water boards—historically, the earliest Dutch regulatory bodies dating back to the 13th century—are to begin working together more closely, so chemical companies will be able to count on more uniform policy.

However, as Quik points out, the covenant covers only the impact of production processes, not of products themselves. Targets for waste reduction, for example, are process wastes, not post-consumer waste.

Reductions are taken from 1985 levels, the base year. "The year 2000 is a solid goal," Quik said, and 2010 is a "guidance" goal. "We assume there will be technology improvements by that time, because we need them to get those [environmental] improvements. We will see, closer to that time, whether we need to modify the targets up or down."

Cees Moons, director of the industry division in the Directorate General for Environmental Protection in the Ministry of Housing, Physical Planning & Environment at The Hague, said the whole process started when a document was issued by the National Institute of Public Health & Environment, called "Concern for Tomorrow," which outlined steps toward a sustainable future. This was in the same wave of movement as the efforts in the late 1980s spearheaded by Norway's Prime Minister Gro Harlem Brundtland, Moons said at a roundtable discussion of the covenant at the VNCI, which included Moons, Quik, and Jan-Willem Biekart, who is with the Stichting Natuur en Milieu, the Foundation for Nature & the Environment.

The Dutch document led to the National Environmental Policy Plan, "To Choose or to Lose," issued in 1989. This document was discussed in Parliament, which agreed on the targets in the plan. These targets were then formulated into a plan to put into effect.

"Then we faced the question of how to execute this plan," Moons said. "We saw two extremes as possibilities to implement the plan," he explained. The government could go just with voluntary agreements with covenants, instead of legislation, or it could go with legislation alone, traditionally the more usual way. "We decided to make a combination of the two. The implementation should be done on a legal basis, to not only give obligations to the companies, but rights and certainties about investments." The law already requires a site to have an operating license, which is subject to negotiation, he pointed out. The covenant would ensure agreement, rather than conflict, and it would give companies a plan to use as a management tool.

Starting with the most serious priorities, the government began the discussion process with two branches of industry—primary metals and chemicals—looking with each at the problems peculiar to that branch. The sessions included representatives from the relevant ministries, municipalities, provinces, water boards, and industry federations.

It was important, Moons emphasized, that all the groups be represented, particularly the provinces and municipalities. "At the end of the process, the results should be laid down in the licenses," he said. "Therefore, we must have commitment from the provinces and municipalities, because they are the ones who grant the licenses. Much negotiation still has to be done at the level of the individual company, but by the covenant there is a framework, so we can see if results are good or not."

And, he added, "it was not an easy process. A good covenant should not be signed too easily. When it has meaning," and people must make a serious commitment, "there should be hesitation in signing it." Moreover, there were some complications from the fact that the first covenant, for the primary metal industry, was held to be the framework for all the remaining industrial sectors. "It did complicate matters for the chemical industry just a bit," acknowledged Moons, "but not too much."

According to VNCI's Quik, "Going through a negotiating process for two-and-a-half years was not time lost. We were creating commitment, and [gaining an] understanding of what the plan meant. We have about 95% support from our members. Had we signed in a month, we would have had more difficulty getting everybody on board."

The Foundation for Nature & the Environment's Biekart brought up the environmentalists' qualms. "Not all that time has been used to gain support from chemical industry," he said. "There was lots of time lost in debating commas and points in the text—that's what [environmentalists] think. And much more time will probably be lost in the future without real action being taken."

He granted that the chemical industry's support for the plan "has been greater than for that of the primary metal industry. You have talked more with your industry," he said to Quik. But Biekart observed that in practice many local governments are saying that, because of the negotiations with companies, they will defer writing new, tougher licenses until the covenant is completed, and they will sharpen the requirements then. "The longer the negotiation, the longer it takes before licenses start to be sharpened—it may be more than a year. Time is an important criterion for us—every year's delay is a year too much for us."

According to Moons, the time taken was the shortest time practicable. The government first had to work out its text, then gain commitment from the industry. Next came the time for discussing provisions of the covenant with provinces and regions. Additionally, the large number of companies in the chemical industry prolonged the time needed. "For the primary metal industry," he pointed out, "one company in particular, Hoogovens, is by far the biggest out of a total of maybe 20 or 30 companies. Hoogovens was willing to sign, to take the lead, and the smaller ones would follow."

The primary metal industry companies were given eight months to develop their individual corporate plans. Based

Dutch chemical industry at a glance

Sales in 1992: $24.6 billion—15% of country's industrial production

Sales makeup: bulk chemicals, 60%, and specialty chemicals, 40%. Sales to European Community, 72%; U.S., 4%; Japan, 2%; and others, 22%

Exports in 1992: $24.1 billion—20% of country's total exports

Imports in 1992: $15.4 billion

Capital spending in 1992: $1.9 billion—25% of country's industrial investment

Production index (1985 = 100): 1991 = 120; 1992 = 122

Employment in 1992: 87,400—10% of country's total industry employment

on the government's experience there, it lengthened the time for chemical companies to 14 months. Besides, he says, "when we get 140 plant site plans, we couldn't do them all at once." And the government is working on plans for the other industries, for a total of eight. The covenant for the printing industry is now signed, and that for the dairy industry is coming up. The covenant for the electronics industry will be finished by the end of this year, while negotiations have started on covenants for the paper, textiles, and meat industries.

The extended time, though, does not please environmentalists. Biekart insisted: "There are a number of examples of licensing being stopped while authorities are waiting. At first, it was only eight months until every signing company would have a site environment plan. Now that has stretched out to 14 months. The time becomes longer and longer, but the results are not certain. We have only the commitment—which is worth a lot, but is not a fact, and does not give a firm grip on the outcome of the process."

Industry had to have time to work out how it can hold up its end of the covenant bargain, Moons responded. "If you look at the year 2010, you must look at process modification and integration. You can't reach the targets with end-of-pipe solutions. You must combine a process-integrated solution with investment plans. Therefore, it must be an open process, with the company supporting the effort. It takes time to do this."

Part of the problem as Biekart sees it, however, is the very nature of those commitments. Although the covenant "in some aspects is very valuable," he acknowledged, "we doubt the commitment. We don't trust industry because we've never had grounds to do so. If companies did these things over the last 10 years, it is because authorities forced them to, it has not been their choice. We want to see that industry commits itself to sustainable development, and that it devotes its creativity to reaching this goal."

And he indicated just a bit of longing for confrontational legal battles. "Our basic criticism is that we are absolutely unsure about what will come out of the effort. Self-regulation is becoming a huge issue. In the U.S., you can ask a judge to clarify the case. In the Netherlands, we have only an administrative judge. We miss the fighting capacity: the [Dutch culture requires] talking, finding agreements, compromising, being reasonable.

"In this, if government gives away any part of its legal position, it is giving away the environment," Biekart said.

"No one is giving away any legal position," Moons answered. Moreover, he sees improvements from the current situation: Environmental groups will get more information, and things will get better.

For Quik, the plan offers no guarantee to the industry. "If you have a guarantee, you would also get a guaranteed license to operate. But we won't—we will still have to get permits, and we might not be able to. The system is reasonably in balance."

Nonetheless, Biekart said, the government "should not be afraid to introduce policy measures stronger than these commitments. I'm not against the covenant—I'm fully aware of the value of this. On the other hand, there are pressing environmental problems, and not just problematic emissions of substances like sulfur dioxide and nitrogen oxides. We think it's necessary to introduce stricter instruments alongside these covenants—a carbon [energy] tax, controls on use of groundwater, and so on."

Such measures are outside the scope of the covenant, and could be more transnational, as well. Meanwhile, VNCI members are now working out how to cope with the covenant. There are two levels of commitment—one by the chemical industry, for which the VNCI signed, and one by the individual companies.

VNCI has about 105 members, of whom about 95 have signed the covenant, covering more than 95% of the industry's emissions. According to Quik, some members have not signed the covenant but will form a plan—some of these might be companies already in legal battles over pollution guidelines, for example, who would not want to prejudice their cases.

Some of the subsidiaries of U.S. companies have signed; others are cautious about signing, but will adhere to the covenant nonetheless. If a company offers no cooperation at all, local authorities can take the initiative to change—by strengthening or even refusing to issue—a license. Quik predicted that ultimately only 1 to 2% of VNCI's members will not voluntarily cooperate.

He said, "We have already told our members that if they run into difficulties with licenses and have not signed, we will find it difficult to support them, at least officially."

The targets in the government plan are based on agglomerated data for the chemical industry. Companies make their plans based on best available technology, and it is up to the government to look at the sum of the plans, to ensure that the totals are approaching the country's goals. Plans are open to public inspection and include an annual progress report.

According to Biekart, this is undoubtedly an improvement, as far as environmentalists are concerned. "It gives us all opportunities, and gives an opportunity to industry itself. This will make it clear: who is far in front, who is behind. It is still to be seen what will be in these plans. For us, this is a minimum only, particularly because the plans are only for production."

Quik said, "For all parties, this is a learning process. The plan is very challenging, particularly in a time of economic downturn." He added, "We think this covenant will be an advantage because it will give companies flexibility. Companies know what they're heading for, given the long-term objectives. You can build accordingly. This gives companies a framework for priorities." □

Key reduction targets set by Dutch environmental plan

	2000	2010
	(% reduction from 1985)	
AIR EMISSIONS		
Benzene	75%	97.5%
Acrylonitrile	50	97
Ethylene	50	90
Toluene	50	90
Vinyl chloride	90	90
Fine particulates	75	95
WATER EMISSIONS		
Benzene	75	90
Acrylonitrile	50	90
Oil	60	90
Nickel	50	80
Zinc	65	80
Lead	65	70
Nitrogen compounds	70	75
Phosphorus compounds	75	90

Source: Declaration of Intent on the Implementation of Environmental Policy for the Chemical Industry

PAPER CHEMICALS

Paper chemical suppliers face strong environmental pressures, major changes in pulp and paper markets

Ann M. Thayer,
C&EN Northeast
News Bureau

Because paper is ubiquitous, it generally is taken for granted. However, paper and paperboard comprise a massive, multibillion-dollar industry employing vast amounts of natural resources, equipment, energy, and chemicals. The U.S. paper industry, with a positive trade balance, has long enjoyed a competitive advantage over competing industries in Scandinavia, other countries in Europe, and Japan.

However, the outlook for profitability in the industry has been bleak since 1991, when earnings plunged almost 25% below 1990's already depressed earnings. In 1992, profit margins for pulp were near zero, and U.S. shipments of paper and allied products grew only 1.5% to more than $126 billion, according to the Department of Commerce. The market continues to be constrained by declining prices, overcapacity, and generally poor world economies. Modest volume growth is expected to continue, with paper shipments growing about 4% in 1993 and continuing to grow about 2.5% per year through 1997.

Papermaking is being affected by federal, state, and local regulations regarding solid waste, air and water quality, and government procurement. Numerous environmental and business groups specifically are targeting the industry to change its production methods, its chemical use, its energy consumption, and its environmental impact. And several pieces of federal legislation—among them the Clean Air Act and the Clean Water Act—are expected to directly affect papermaking through new emissions standards.

Environmental and economic pressures, along with shifting consumer demands, have been changing the way paper is manufactured. However, many industry observers say that, at a time when the paper industry is so depressed, papermakers have been slow to capitalize process and equipment changes, taking these steps only when they have been absolutely necessary. Pulp and paper industry capital spending was down about one third from a record level of 1990 to $11.3 billion in 1992, says Commerce, with environmental capital spending accounting for 11 to 12% of the total.

Still, major changes have been occurring in the chemistry of each step of the papermaking process, leading most chemical suppliers to a more positive outlook than their paper industry customers. Changes arising from concerns over paper mill effluents, recycled paper content, and conversions from acid to alkaline papermaking generally are pushing an overall growth rate in many chemicals to at least twice that of the paper industry.

The market for pulp and paper chemicals is estimated to total more than $4 billion, or about $100 worth of chemicals for every ton of pulp produced. Demand for pulp and paper chemicals is expected to grow 6% annually to $4.8 billion in 1995, according to the Cleveland-based marketing research firm Freedonia Group. However, the greatest barrier for chemicals will be any related capital costs for new processes.

Papermaking elements

However large and complex the papermaking process and industry are, most of their constituent elements are represented in a single sheet of paper. The basis of most paper is wood fibers from pulp produced by chemical or mechanical means, or a combination of the two, depending on the desired grade of paper. Pulp production, often using large amounts of caustic soda (NaOH), is only the first in a several-step process involving myriad commodity and specialty chemicals.

Paper rolls await shipment at completion of papermaking process

The pulp used to form a sheet of paper also may include fibers from recycled paper—either paper mill scrap or consumer waste. The recycled paper content is expanding primarily because of concerns about the disposal of municipal solid waste. In 1992, 33.6 million tons, or more than 38% of paper and paperboard production, were recovered for recycling or export. Of this recovered amount, 26.2 million tons made up 30% of pulp raw materials used in new production, according to figures from the Washington, D.C.-based American Forest & Paper Association.

In 1993, the amount of paper recovered is expected to reach 36.7 million tons, with 29 million tons reused domestically. The U.S. paper industry has set a goal to recover 40% of all paper used by 1995. As the recycled content of paper increases—and the presence of weakened reprocessed fibers—so too does the need for new chemistries and processing chemicals. To use these secondary fibers, many different chemicals are needed to remove inks, to bleach, and to separate out the nonfiber components of recycled paper.

Whatever the source, fibers usually are bleached in the next step of the papermaking process if they are to be used in high-grade paper applications. The most common bleaching chemicals are chlorine and chlorine dioxide. However, moves away from chlorine chemicals because of environmental pressures on the control of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8-TCDD) and chlorinated organics in paper mill effluents are increasing the use of other bleaching agents such as hydrogen peroxide, oxygen, or ozone.

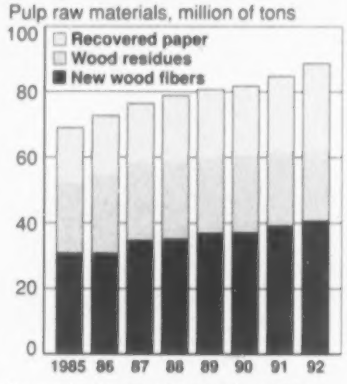
To replace expensive pulp, as well as provide opacity and dimensional stability, the clean fibers may be mixed with mineral fillers and pigments such as calcium carbonate, kaolin, or titanium dioxide. Binders and sizing materials such as latexes, starch, rosin, and synthetic polymers retain the fillers or add water repellency, a useful property for printing with water-based inks.

Processing aids—primarily polymer based—that increase fiber retention and drainage, or contribute wet or dry strength, are added before a sheet of paper is formed. The fiber and chemical mixture is then laid out on a wire mesh to allow for water drainage, pressed, dried, and generally mechanically finished.

Coatings, again often mineral-based, also may be used to give paper its finished appearance, such as on this sheet of magazine paper. A desire for lower weight papers, to decrease shipping and postal costs, and an increase in the use of four-color printing are expanding the use of coatings to ensure the opacity of thinner sheets and the finish required for color printing. Depending on the application, other polymer or wax coatings may be applied to paper for moisture resistance.

The most significant chemically related change in recent years has been a move from acid to alkaline papermaking, which has spurred growth for specialty chemicals and fillers. Acid or alkaline refers not to the pulping process, but rather to the residual pH of the paper at the time a sheet is formed. Alkaline paper is valued more because it lasts longer, is less susceptible to yellowing, and allows for greater amounts of pulp-replacing fillers. The majority of paper in the U.S. now is produced under alkaline conditions.

Recovered paper adds to pulp raw materials



Source: American Forest & Paper Association

Pulp chemicals market to grow

The goal of pulping is to reduce wood to cellulose fibers while removing lignin, a natural resinous adhesive. Pulp produced from hardwoods (deciduous trees) tends to have shorter, weaker fibers, compared with that from softwoods (coniferous trees). Traditional mechanical or chemical, or newer combinations such as thermomechanical or chemothermo-mechanical, processes can be used to produce pulp. Mechanical, also called groundwood, methods produce extremely high yields of less pure and less expensive pulp, used extensively in newsprint. Although the yields are lower, by about 50%, chemical pulping methods produce a much cleaner, stronger pulp.

In simple terms, chemical pulping can be divided into processes based on caustic soda and sulfates, or sulfites. Sulfite pulping involves boiling wood chips in an acidic solution. In the kraft process, also called the sulfate process because of the addition of sodium sulfate to aid in digestion of the pulp, wood chips are heated in a caustic liquor. More than 80% of pulp made in the U.S. is from the kraft process. As the strongest pulp, unbleached kraft pulp commonly is found in corrugated cardboard and paper bags.

Kraft pulping also is attractive because it is more energy efficient than other processes, and it can be operated in a closed loop in which almost all of the caustic soda is recovered. However, the kraft process, as well as other pulping methods, has come under environmental scrutiny because of emissions and effluents, toxic residues or materials that must be disposed of, or the need to further bleach the pulp.

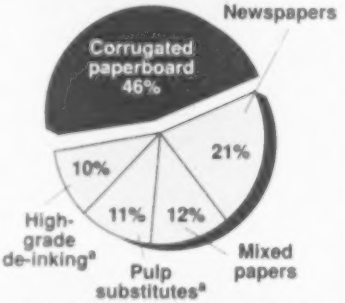
Traditionally, pulp and papermaking companies have been major customers for chlorine and caustic soda, coproduced by an electrolytic process that yields 1.1 tons of caustic soda for each ton of chlorine. Consequently, papermakers have become known as electrochemical unit—ECU—buyers. Major chlor-alkali producers include Dow Chemical, Occidental Chemical, Georgia Gulf, Olin, PPG Industries, and Elf Atochem.

The paper industry is the single largest market for caustic soda, accounting for about one quarter of total production. Caustic soda use in the industry is expected to grow very slowly over the next five years, about 1% or so per year, says Roger E. Shamel, president of Consulting Resources, Lexington, Mass., from the present level of about 2.7 million tons per year. However, the simultaneous shift away from chlorine as a pulp-bleaching chemical is expected to contribute to a chlor-alkali imbalance within the paper industry, on top of the already cyclical chlor-alkali markets.

Chlorine, which follows the general economic cycle, currently is expensive, explains Shamel, and caustic soda, which lags the cycle by six months or so, is relatively cheap—a situation that was reversed only a year ago. ECU buyers generally receive more favorable pricing in buying both coproducts. And, although ECU buyers are nearly ideal, stable customers for chlor-alkali producers, the situation is not expected to continue as a higher ratio of caustic to chlorine becomes needed by the paper industry.

"The ratio of out-of-balance [non-ECU] caustic to ECU caustic is changing radically," says Billy Tullos, Philadelphia-based Elf Atochem North America's chlor-alkali business manager. "The demand for chlorine in pulp and paper production is declining while caustic is maintaining its volume at near historical levels." Many producers suggest that demand for chlorine in other areas, such as polyvinyl chloride, will keep overall chlor-alkali markets in balance. This balance ultimately will depend on if or how soon legislation or environmental moves force phaseouts of chlorine in other areas such as chlorinated solvents and chlorofluorocarbons, as well as in pulp and paper.

Paperboard is 46% of recovered paper wastes



1992 total recovered paper and paperboard = 33.6 million tons

a Includes ledger, tabulating cards, bleached sulfate paper shavings, envelope and bleached sulfite and sulfate paper cuttings, coated book stock, and computer printout. Print-free grades are reported as pulp substitutes. Printed grades, if de-inked, are reported as high-grade de-inking. Source: American Forest & Paper Association

Soda ash opportunity

Alternative sources of caustic, other than ECU caustic, are one solution to meet the projected long-term shortfall. Shamel points out that there may be better opportunity for soda ash (sodium carbonate) as a substitute alkali, not in the immediate future, but later this decade when ECU caustic prices become high. Soda ash demand in the paper industry currently has been flat because of low caustic prices, but could grow 6 to 7% per year over the next few years, from a current fairly low basis of about 200,000 tons per year.

Soda ash may be used directly as an alkali or used, as is trona ore, to produce caustic soda which is then referred to as "chemical caustic." "The [chlor-alkali] cycle is expected to reverse itself again and so chemical caustic may indeed make sense in another couple years," says Shamel. "Caustic soda [supply] will be relatively tight again and that's when you will see either more of this direct use of soda ash or the startup of chemical caustic plants." Most chlor-alkali producers expect to see prices tightening up in mid to late 1994.

Soda ash generally offers two major advantages, economics and quality, as a substitute alkali in pulp liquor makeup, explains James B. Coward, pulp industry manager in FMC's alkali chemicals division in Philadelphia. On site at

a paper mill, soda ash can be added directly in the causticizing process to form, on reaction with calcium hydroxide, caustic soda for pulping. Soda ash also may have potential in the on-site production of precipitated calcium carbonate, which is used as a paper filler, as a coproduct with chemical caustic.

Several conversions have been driven solely by quality issues, specifically the lower chloride content of soda ash, which is some 40 times less than regular-grade (diaphragm) caustic soda, says Coward. Excessive chloride in the pulp liquor recovery cycle not only acts as a corrosive agent but can lead to equipment problems and increased maintenance demands as well. However, a major impediment to switching to soda ash is the need for excess causticization capacity, generally not available at older mills.

Most recycled paper and paperboard are used again for similar products

Recycle end use	Corrugated cardboard[a]	Newsprint	High-grade papers[b]	Mixed paper
Containerboard	55.5%	3.1%	4.0%	4.7%
Paperboard	22.6	20.7	9.8	41.9
Newsprint	0	32.6	0	5.9
Tissue	0.6	7.4	33.4	12.0
Printing/writing paper	0	0.7	28.7	1.8
Other	3.2	17.2	3.6	11.7
Exported	18.1	18.2	20.5	21.9
1992 TOTAL, millions of tons	**15.4**	**7.3**	**7.1**	**4.0**

a Includes kraft paper and bags. b Includes high-grade de-inking and pulp substitutes such as ledger, tabulating cards, bleached sulfate paper shavings, envelope and bleached sulfite and sulfate paper cuttings, coated book stock, and computer printout. Print-free grades are reported as pulp substitutes. Printed grades, if de-inked, are reported as high-grade de-inking. **Source:** American Forest & Paper Association

On an economic basis, average caustic soda prices exceeded $265 per ton FOB (free on board, or without fees for delivery to or loading on carrier) in 1990 through 1991 and may reach that level again by 1996. By comparison, soda ash—on an equivalent chemical basis—is about $130 per ton FOB at list price. Depending on the exact pulp mill location and application, says Coward, economics favor soda ash if caustic soda prices exceed $165 to $200 per ton delivered.

Chemical caustic is produced by three companies—FMC, Solvay, and Elf Atochem (in a joint venture with Texasgulf)—which each have a plant in Wyoming. However, these plants generally are running at only minimal rates, says Shamel. "Caustic prices are so low that once you make chemical caustic in Wyoming and ship it to market, producers can't compete with electrolytic caustic."

Tullos says Elf Atochem saw the trend toward non-ECU caustic several years ago and strategically decided to have a source of chemical caustic soda

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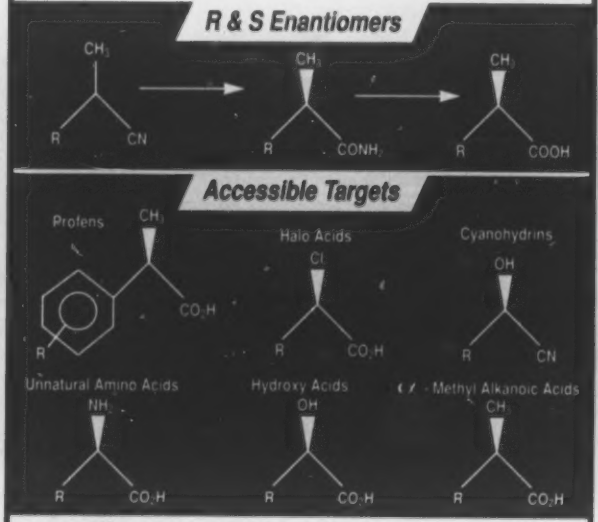

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available to the pulp and paper industry. "It allows the company to supply all the caustic soda that the pulp and paper industry customers might require regardless of whether there is a home for chlorine," he says, "and the company is not tied to the viability of a companion product which is being used less and less."

Chlorine use is dropping

Chlor-alkali producers have differing views on whether or when a phaseout of chlorine will occur in the pulp and paper industry. Some producers predict chlorine will be phased out by the end of the decade, whereas others suggest its use will decline and eventually level off. There even is disagreement on the rate of decline, ranging from a few percent to as high as 10% per year. Deciding factors will be the success of ardent environmental groups in their moves against chlorine, new regulations poised to come out, and consumer demands for chlorine-free paper.

Pulp and paper chemical markets to grow 6%

$ Millions	1990	1995	% annual growth
Papermaking chemicals	$1326	$1800	6.3%
Paper additives	900	1250	6.8
Pulping chemicals	729	915	4.6
Bleaching chemicals	657	875	5.9
TOTAL	$3612	$4840	6.0%

Source: Freedonia Group

Chlorine is by far the most widely used and largest volume pulp-bleaching chemical. For pulp to be used in most applications, such as the large markets for uncoated sheets of white paper or coated pages, it must be treated further to remove lignin and then generally is bleached. Overall, North American demand for pulp-bleaching chemicals—chlorine, sodium chlorate, hydrogen peroxide, and others—is expected to increase 2.6% per year to about 4 million tons in 1996, reports Freedonia Group.

Currently, about 1.2 million tons of chlorine, or about 9% of total production, are used annually in paper manufacturing. Chlorine's success has been based on the fact that it is inexpensive, extremely effective, and does not degrade the pulp. Its decline has been primarily because of environmental and regulatory limitations.

About 95% of mills use chlorine for bleaching, says Leslie Littell, chlorine product manager at PPG Industries, Pittsburgh, with usage declining 8 to 10% per year. In the U.S., on a relative basis, essentially no totally chlorine-free (TCF) paper is produced. Only a handful of mills produce small quantities of TCF paper as compared with a higher percentage in Europe. A larger number of U.S. mills are moving toward elemental chlorine-free (ECF) paper in which chlorine dioxide, rather than chlorine, is used as a bleaching agent.

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"What will affect the industry the most is the legislation to come out," says Littell. How strict the limits are on chlorinated organics and 2,3,7,8-TCDD will determine pulp and paper mills' abilities to meet regulations and afford the additional costs. "Some of PPG's customers say that as many as 12 to 15 mills could shut down because they are not making money now and they don't have the money to put in [new technology that may be] required to meet regulations," she says.

On the governmental front, attention has focused on executive orders being finalized by the Clinton Administration. At various times and to various degrees, these proposed orders have dictated government procurement of TCF paper, recycled fiber content, and "environmentally preferable" products. The U.S. government purchases between 1 and 2% of the more than 20 million tons of total U.S. printing and writing papers manufactured.

In late October, an executive order was issued directing federal agencies and the military to buy paper with at least 20% recycled content by the end of 1994, and 30% by 1999 (C&EN, Oct. 25, page 19). But, the Administration's stand on chlorine has eased, with the executive order only relaxing federal standards on paper brightness rather than requiring the purchase of TCF paper.

Other groups also are looking at procurement questions. This summer, the Paper Task Force was established to develop a market-based approach through which it can influence the way in which paper is produced, purchased, and used in the U.S. The seven organizations involved—Environmental Defense Fund (supported by the Heinz Family Foundation), Duke University, Johnson & Johnson, McDonald's, NationsBank Corp., Prudential Insurance, and Time Inc.—together purchase more than $1 billion of business printing and writing, publication, and packaging paper products.

Hoping to develop recommendations for increasing the use of "environmentally preferable paper and paperboard," the task force initially did not stress any preconceived definitions. Instead, its members are to assess their own needs and specifications for paper and paperboard with final purchasing decisions to be driven by a "comprehensive consideration of scientific and economic information on the environmental effects of paper production, use, recycling, and disposal." Analysis will include recycled and virgin papers, and papers produced by various pulping and bleaching technologies.

Task force members say they will work closely with their paper suppliers, as well as seek the views of experts in the pulp and paper industry, environmental and economic groups, and academia. In addition to changing its own members' use of certain paper products, the Paper Task Force hopes to design a purchasing model applicable to a broad range of organizations. A report is to be published in about a year.

Pressures on chlorine use

Both the Canadian and U.S. governments are issuing or pursuing regulations that focus on pulp and paper mill effluents. And, the International Joint Commission between the U.S. and Canadian governments, which advises the governments on issues concerning

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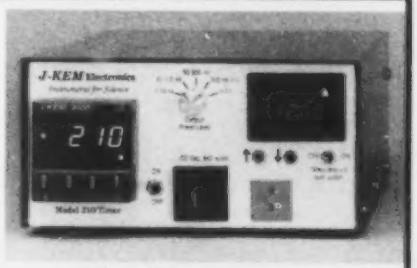

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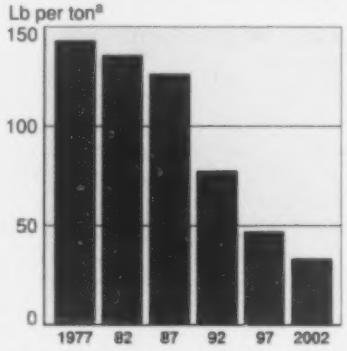
Chlorine use in U.S. pulp production is decreasing



a Estimated pounds of chlorine used per ton of bleached and semi-bleached kraft pulp
Source: Probe Economics

the Great Lakes region, has recommended eliminating chlorine in industrial processes. In the U.S., reauthorization of the Clean Water Act, Clean Air Act, and Resource Conservation & Recovery Act all are expected to have some impact on the pulp and paper industry.

A new bill, H.R. 2898, entitled the Chlorine Zero Discharge Act of 1993, has been introduced in Congress. This bill calls for an amendment to the Clean Water Act to completely eliminate discharges of chlorine compounds. It also specifically would ban the use of any chlorinated bleaching agent in the pulp and paper industry to prevent the formation of chlorinated organics. Chlorinated organics, the larger chemical family of which 2,3,7,8-TCDD is a member, have been targeted because of their persistence in the environment, tendency to bioaccumulate (accumulate in living organisms), and detrimental impacts on the environment and human health.

However, there is an ongoing debate over the full effect of chlorinated compounds (C&EN, April 19, page 11, and May 31, page 19). In addition to economic arguments that the chlorine industry has put forth against the phaseout of chlorine (C&EN, May 10, page 11), the Chlorine Chemical Council—a joint informational effort of the Chemical Manufacturers Association and several other trade associations—and the Chlorine Institute are still working to publish a massive report covering 150,000 different studies on the health and environmental effects of chlorinated organics.

Greenpeace, which is opposed to chlorine use in any industry, argues against using any chlorinated compound, not just elemental chlorine, in paper manufacture. The group asserts that there are an increasing number of ways to make high-grade paper without using chlorine that are not being practiced in the U.S. Mark Floegel, U.S. pulp-paper campaigner for Greenpeace, believes that the paper industry is trying to control demand for TCF paper by keeping such products off the market.

"The pulp and paper companies are not making any money and they don't want to spend money to recapitalize their mills until they absolutely [have to]," he says. "There also is a liability issue—to shift away from using chlorine is a tacit admission that chlorine is bad." He stresses that being chlorine free will not only reduce the presence of chlorinated organics in effluents, but also will allow pulp and paper plants to close process loops, recover chemicals, and reduce fresh water use. "I think it is inevitable that the industry is going to go chlorine free because the environmental benefits are too huge to ignore."

However, the Washington, D.C.-based Chlorine Chemical Council says that TCF manufacturing is not a proven technology in bleached kraft pulp mills and that the environmental impact of TCF mills and paper is largely unknown. Chlorine producers and industry groups say that, with careful process controls, pulp and paper mills can use chlorine, often in combination with chlorine dioxide, and meet current regulations on 2,3,7,8-TCDD and chlorinated organics. Changes in paper manufacturing processes at modern mills have brought about reductions as high as 90% in the amount of 2,3,7,8-TCDD produced, says Brad Lienhart, managing director of the Chlorine Chemical Council.

Accordingly, the industry argues against the presumed benefits from TCF manufacturing and its relative costs—estimated to be as high as $13 billion in capital costs, $700 million in added operating costs, and nearly $2 billion in lost chemical business. Industry observers also question the ability to competitively produce high-brightness pulp with equivalent properties without chlorine bleaching. They also raise the possibility of adverse impacts on energy consumption and product recyclability.

In late September, 14 U.S. and Canadian chemical manufacturers and forest products companies formed the Alliance for Environmental Technology (AET). AET's mission is to "promote practical, proven advances in the environmental performance of modern papermaking, and to achieve sound Canadian and American federal, state, and provincial policies." The group hopes to address current policy debates in both countries that will influence the future of the North American pulp and paper industry.

Moves to chlorine dioxide

The Environmental Protection Agency will shortly announce its recommended rulemaking for pulp and paper effluent guidelines. The guidelines are the result of what has been called the "cluster rulemaking," a year-and-a-half-long investigation during which EPA simultaneously examined regulations covering different environmental media. The pulp and paper industry, which participated with EPA, industry, and environmental group representatives, was selected to be the first target of such rulemaking, according to Lienhart.

The proposed rules are to be followed by a two-year comment period. During that period, explains Lienhart, there also is a commitment to research—on how existing process changes are working

Use of pulp-bleaching chemicals in North America shifts away from chlorine

Thousands of tons	1985	1991	1996	% annual change 1991–96
Chemicals				
Chlorine	2,152	1,828	1,310	–6.4%
Sodium hydrosulfite	35	45	50	2.1
Sodium chlorate	680	1,157	1,830	9.6
Hydrogen peroxide	61	158	250	9.6
Oxygen and others	110	250	460	13.0
TOTAL CHEMICAL MARKET	**3,038**	**3,438**	**3,900**	**2.6%**
TOTAL PULP PRODUCTION	**36,214**	**40,565**	**44,700**	**2.0%**

Source: Freedonia Group

Union Camp photo

This pulper recycles an average of 500 tons of wastepaper per day

and on resulting effluent streams—as part of a continuing discussion on optimum process configurations. Once finalized, compliance with the rulemaking is expected to begin Oct. 31, 1995.

The rulemaking will offer what is generally viewed as a compromise for the pulp and paper industry. It is expected that limits to be set on air and water emissions can be met by using chlorine dioxide, instead of chlorine, in bleaching processes. According to Greenpeace, chlorine dioxide produces about one sixth the amount of chlorinated organics as does chlorine.

"The option of a heavy substitution of chlorine dioxide for chlorine would be a workable option that gets the industry to a point where it meets [standards], enhances recovery technologies, essentially eliminates the concerns about effluents, and still allows the industry to make top quality products that are recyclable, energy efficient, and competitive globally," says Lienhart. "However, this carries with it a not insignificant price tag of about $6 billion [in capital investments] and increases the operating costs to the pulp and paper industry by $300 million a year."

AET also supports chlorine dioxide use as a technology for eliminating toxic pollutants from papermaking. "Lost in the 'crusade against chlorine' is the recognition of the superior performance of chlorine dioxide," says Doug Pryke, executive director of AET. "This process alternative—whose chemistry is fundamentally different from chlorine gas—is without rival both in terms of environmental performance and product quality.

"What we know about chlorine dioxide is surpassed only by what we do not know about the TCF alternatives. Apart from chlorine dioxide, all the other alternatives are virtual unknowns from an environmental standpoint."

However, Greenpeace disagrees and does not expect to be pleased with the rulemaking, asserting that chlorine dioxide is an entirely unacceptable alternative. "Because less chlorine is being put in the front end, of course, you are getting fewer organochlorines out the back," says Floegel. "But, because these are persistent chemicals, they won't go away once they are produced and will continue to build up in the environment.

"Chlorine dioxide is not the answer. It is a bad investment. It is a false investment. It doesn't solve anything, it only delays the problems. The real investment is to be completely chlorine free." Floegel believes the expense of converting to chlorine dioxide technology will have significant ramifications in the future. "By forcing the paper industry into a chlorine dioxide mode," he says, "EPA is locking them in because ... industry is not going to want to change [technologies] until the investment has been amortized.

"Then there are two possible outcomes: In a couple of years, either the industry is going to have to spend a lot more money to go completely chlorine free, which means they will be very angry and upset, or EPA will not force industry to get rid of the chlorine dioxide technology, and the environment and human health are going to be paying a toll for it 20 to 30 years down the road."

Growth for chlorate

Many mills have already invested in alternative bleaching technologies with some estimates for conversion to chlorine dioxide as high as 50 or 60% of bleaching operations. Chlorine dioxide is produced on site at paper mills from sodium chlorate. Thus, the continuing conversion to chlorine dioxide has been a boon for sodium chlorate producers, because more than 90% of sodium chlorate production goes to the pulp and paper industry.

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Moves away from chlorine are viewed favorably by producers of substitute chemicals, says Shamel of Consulting Resources, because all of the alternatives cost more than chlorine and in general offer higher profit margins. Chlorate markets have been growing at double-digit rates and likely will continue to grow at nearly the same rates over the next few years. However, adds Shamel, producers have built excess capacity because many of them believed that the conversions would occur more rapidly than they have.

Major sodium chlorate producers in the U.S. include Eka Nobel, Elf Atochem North America, Kerr-McGee, and Occidental Chemical. Kerr-McGee, Oklahoma City, doubled its annual capacity for sodium chlorate to 123,000 tons in the second half of 1991 and operated at 80% capacity in 1992. In 1992, the company's sales volume for sodium chlorate climbed more than 35% from 1991. In the short term, the company predicts an annual market growth of about 8%, leveling off to about 3% over the longer term.

By the mid-1990s, says Freedonia Group, higher capacity utilization is expected to cause a strengthening in sodium chlorate prices. Freedonia Group sees overall sodium chlorate markets growing, primarily from demand in pulp bleaching, at about 10% per year from 1.2 million tons in 1991 to about 1.8 million tons by 1996.

Growth may slow in the future as conversions from chlorine to chlorine dioxide near completion. In addition, many industry observers believe that as a chlorine derivative itself, sodium chlorate may only be a short-term replacement for chlorine since demand for TCF paper products may spark a second round of bleaching chemical replacement late in the decade.

Bleaching alternatives

Despite sluggish pulp markets, other pulp-bleaching agents also are gaining in use. As in chlorination, the oxidation of lignin-containing compounds by hydrogen peroxide, oxygen, or ozone, followed by solubilization and extraction, removes the materials that add color or cause fibers to darken. Much of the overall growth in pulp-bleaching chemicals is anticipated to come from those chemicals whose use is driven by environmental benefits.

But the market has not been willing to accept a decrease in pulp brightness or strength, says Don Magid, senior business manager at Solvay Interox, Houston. Only a limited number of pulp and paper operations have converted to newer technologies, often on a pilot or trial basis, he says, because full-scale, continuously operating conversions would involve additional costs. However, as new processes become better understood, more widely used, and incorporated into new plant designs, the costs likely can be reduced. Other economic factors to be considered, he adds, are environmental liabilities and benefits realized in the marketplace.

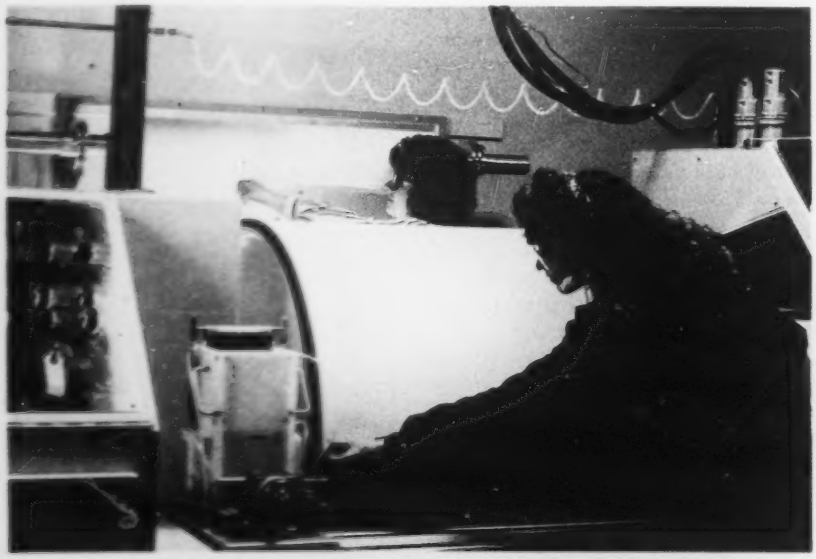
As the move away from chlorinated compounds continues, says Magid, the most probable solution will not be a single technology, but rather a combination of processes that will depend on a mill's specific needs. For example, combinations of hydrogen peroxide, ozone, and oxygen delignification can be used to produce TCF pulp, or chlorine dioxide and oxygen delignification for ECF pulp. Hydrogen peroxide producers also are developing specialty bleaching technologies based on peroxygen chemicals such as peracetic acid, peroxymonosulfuric (Caro's) acid, and formamidine sulfinic acid (FAS).

Among the different delignification and bleaching processes, oxygen and chlorine generally are the least expensive options, says Ron Scheff, manager of peroxygen products at Du Pont, Wilmington. Initially, hydrogen peroxide was marketed as a cost-saving replacement for chlorine dioxide, but comparative costs have become very mill dependent, owing to upgrading in mill design and in bleaching technologies.

Because hydrogen peroxide decomposes into oxygen and water, it is considered among the most environmentally favorable pulp bleaches. Traditionally, it has been used to bleach mechanical and chemothermo-mechanical pulp and as a later-stage brightening agent for chemical pulp. Often, when having to convert from chlorine, says Scheff, paper mills commonly use their available chlorine dioxide capacity for early bleaching stages and, rather than invest in additional capacity, use hydrogen peroxide in later stages.

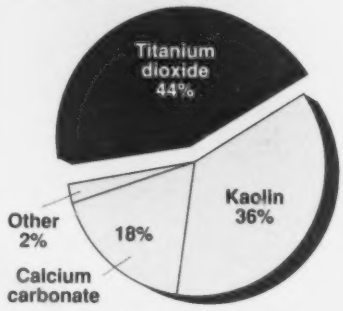
In addition to moves away from chlorine, increases in the use of hydrogen peroxide in other paper areas are helping to drive growth. Market demand is estimated by producers to continue growing at double-digit rates. Freedonia Group estimates the market will grow about 10% per year, from 158,000 tons in 1991 to 250,000 tons in 1996. Major hydrogen peroxide producers include Du Pont, Degussa, Eka Nobel, FMC, and Solvay Interox.

Although growth for hydrogen peroxide in the area of mechanical pulp has begun slowing, says Ken Blackburn, North American pulp and paper marketing manager for FMC's peroxygen chemicals division, its use is growing rapidly in the evolving recycled paper area. Also in the chemical pulp area, its use is projected to begin accelerating over the next few years in re-



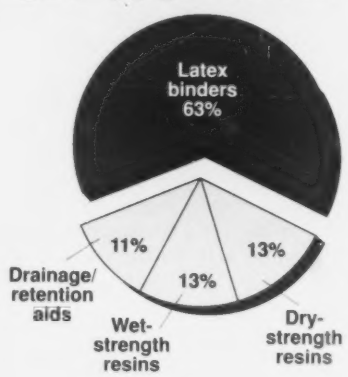
Researcher tests new paper coating at Air Products laboratory

TiO_2 leads mineral markets for paper . . .



1992 North American consumption = $1.2 billion

. . . and latex binders lead specialty paper chemicals



1992 North American consumption = $780 million

Source: Kline & Co.

sponse to environmental and brightness demands. But, adds Blackburn, facing the industry is the fact that hydrogen peroxide demand is quickly catching up with supply, leading to an anticipated supply-demand tightness in 1994.

Less than one fifth of the market for hydrogen peroxide used in making pulp and paper is consumed in processing secondary fibers. But this amount is expected to increase as more recycled paper facilities come on line in the next several years. Because the supply of recycled paper often is a combination of, for example, both newsprint and mixed office waste, chemical suppliers say hydrogen peroxide can be used to prevent alkaline darkening and increase brightness.

FMC has been helping the paper industry reach its targets in recycling different paper grades. In particular, because of competition for higher quality material to be recycled, the company has been helping manufacturers evaluate the trade-offs between switching to lower value materials and increasing chemical use to reduce costs.

Oxygen offers promise

Oxygen continues to be attractive for reducing the need for bleaching chemicals. Rather than act as a traditional bleaching agent, oxygen can delignify pulp and remove the color-containing elements. Other approaches to delignification include extended pulp cooking or the addition of enzymes. Oxygen delignification is becoming more common as an early pulping step, followed by chlorine dioxide, hydrogen peroxide, or ozone treatments.

The current total U.S. oxygen market in pulp and paper is about 1800 tons per day, says Stewart Mehlman, marketing manager for pulp and paper at Praxair, Danbury, Conn., and it is expected to rise to 2200 tons per day in five years. On-site paper mill generation of oxygen accounts for about 45% of oxygen consumed in papermaking and is expected to rise to 90% in five years. This trend can be attributed largely to the cost-effective combination of increased oxygen use at mills and to noncryogenic production methods that reduce production costs.

Oxygen delignification or ozone-bleaching processes may entail considerable capital costs, but oxygen suppliers say that operating costs can be less than those for other chemicals. "Realistically, it's a fairly inexpensive solution to reducing the amount of chlorinated organic discharges," says Dave Park, pulp and paper industry manager at Air Products & Chemicals, Allentown, Pa. "The company is working on a number of technical approaches to facilitate the reduction of chlorine compounds in both kraft pulp, through extended delignification with oxygen, and in secondary fiber."

Air Products has been working for several years on a group of processes that the company calls Oxypro O_R. "Recently, Air Products has accelerated its efforts to introduce oxygen-based processing into recycled fibers," says Park. The company has one commercial installation and a number of trials under way. "The use of oxygen in recycled fiber is ready to take off. Oxygen is a good base approach to be totally chlorine free in recycling paper."

The goal in recycled fiber is not to delignify, but to clean and brighten, Park explains, especially if dealing with office waste that is extensively delignified, white paper anyway. Oxypro is useful as a cleaning and brightening process for color stripping and for removing laser-printed ink and other kinds of dirt or contaminants, such as adhesives found in wastepaper. The process, he says, allows for economical processing and upgrading of mixed papers.

In general—not just for pulp and paper—oxygen capacity in the U.S. is "on the tight side," says Park, and demand for oxygen is growing in delignification processes and is expected to grow in the generation of ozone for bleaching pulp and paper. Praxair, Air Products, and other industrial gas producers such as Airco are looking to supply ozone technology for the pulp and paper industry. However, growth in ozone in the U.S. is pretty slow, says Park. Only one U.S. paper mill has an ozone system in operation today, and it still uses a final chlorine dioxide bleaching step. With little

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commercial and technical experience to date, ozone is not expected to make inroads until the second half of the decade.

Fillers add whiteness

Pigments or fillers can also add whiteness to paper. Recently, the use of pigments and fillers has picked up because of the trend toward lower weight coated papers, such as those used in magazines. This type of paper requires added materials for opacity and whiteness, and the desire for better quality graphics and four-color printing also increases the need for mineral-based surface coatings. During the next few years, the market for pigments and fillers is expected to grow several percent per year overall, but not all at the same rate for all mineral products.

The most commonly used pigment for opacity is titanium dioxide, with major producers including Du Pont and SCM Chemicals. The paper industry accounts for about 25% of the North American market for titanium dioxide, or about 250,000 tons, says Rob Johns, titanium dioxide market manager for paper at Du Pont. "The market grew about 2 to 3% in 1992 and about the same in 1993 ... and should continue to grow at that rate over the next four to five years."

Both titanium dioxide and kaolin producers experienced slow growth when the U.S. paper industry shifted to alkaline papermaking, which boosted markets for calcium carbonate at the expense of other fillers. Because calcium carbonate is stable at high pH, the shift allows this filler to be used. And, because alkaline processes produce a stronger sheet of paper, greater amounts of fiber could be replaced with less expensive fillers. At the same time, changes in precipitated calcium carbonate production that have recently reduced its cost—now about $130, or one half to one third the price of pulp it can replace—caused the market to flourish at double-digit growth rates, 10 to 15% annually, and helped further drive acid-to-alkaline conversions.

Du Pont worker inspects bleached pulp

"On an absolute basis, there was some reduction in titanium dioxide use as the industry went from acid to alkaline papermaking over the past six years," says Johns, "especially in the late 1980s when [the change] really got rolling. ... But we believe that the alkaline conversions are pretty much complete and, thus, the impact on titanium dioxide, from this point going forward, should be minimal." Estimates for acid-to-alkaline conversions run as high as 80% of uncoated free-sheet (office, printing, computer, and writing) paper, and 90% of the coated free-sheet (catalogs, advertisements, annual reports) paper markets.

Johns argues, however, that titanium dioxide's value is greater than for other materials, since it offers the highest degree of opacity. Titanium dioxide is finding increased application in upgrading the quality of recycled paper, since weaker recycled fibers will limit the amount of other fillers.

The U.S. market for calcium carbonate in the paper industry, which is about 1.5 million tons per year, is dominated by Mineral Technologies, New York City, a spin-off of Pfizer, which began building the first satellite production units—located at or near major paper mills—for calcium carbonate in the mid-1980s. These plants produce a high grade of precipitated calcium carbonate using lime and carbon dioxide from a mill's own stacks. Mineral Technologies now has at least 34 plants across the world.

A recent trend has been the further modification of products to allow for increases in filler loadings, explains Walter Nazarowicz, Mineral Technologies' president for minerals. In the U.S., fillers currently are used at about 14 or 15% by weight, but this amount is expected to increase. In Europe, where pulp prices are higher and more stronger fibered softwood pulp is used, as much as 20 or 22% of a sheet of paper may be filler. Mineral Technologies is developing two other new forms of calcium carbonate. The first, called Ultrapaque, will compete with titanium dioxide as an opacifier; the second, unnamed, material can be stabilized under acid conditions.

Calcium carbonate also competes with kaolin in filler and coating uses. The largest kaolin producers for paper are Engelhard and English China Clays. Kaolin is available in a wide variety of grades and costs, depending on the particular application. Lower grade kaolin is used as a filler, whereas higher grade kaolin is used to provide the gloss of surface coatings. One of the advantages of kaolin is that it can be

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used in acid or alkaline papermaking conditions.

The kaolin market has been fairly static, says Ray Downey, director of marketing for paper pigments and fillers at Engelhard, Iselin, N.J., although there has been some growth in calcined kaolin coating grades, where the company focuses much of its business. "Growth for kaolin is down to about 2% per year, and that is the projection from now until the end of the century," he says, primarily because of competition from calcium carbonate and continuing acid-to-alkaline conversions. The U.S. market volume for kaolin is about 5 million to 7 million tons per year.

Positive trends for kaolin include paper recycling and an increased use of color printing in newspapers, says Downey. Historically, the newsprint market, based largely on groundwood pulp, used very few mineral fillers. "In the last few years, [newsprint producers] have been looking at adding minerals to improve brightness, printability, 'strike-through,' or other ink-related problems," he says. "But they usually are not set up to handle minerals very well and they want to add as little as possible while getting the most for their money. And that's meant growth in the calcined kaolin area for the last three years."

Need for binders is up

As the amount of minerals in alkaline paper increases, so too does the need for binders to hold fillers in place or in coatings. Increased recycled fiber content has required binder suppliers to develop technologies that accommodate the complications presented by recycled fibers. As more pigments are used to compensate for lower brightness fibers, the use of binders also will grow. Recycled fibers can add to the roughness of the paper and require binders and pigments in coating formulations for good smoothness.

Binders used in papermaking generally are latex, starch, protein, or specialty polymers. Polyvinyl acetate and other vinyl acetate resins are produced by manufacturers such as Air Products, Rohm & Haas, Union Carbide, Reichhold Chemicals, and National Starch & Chemical.

Product availability has been good for all emulsion products for coating binders, says Daniel Tafaro, marketing manager for paper at Air Products, and a slight upward trend in pricing is expected in the next year or two. To expand its polyvinyl alcohol-based products, Air Products is offering new products for optical brightening applications and for protein binder replacement.

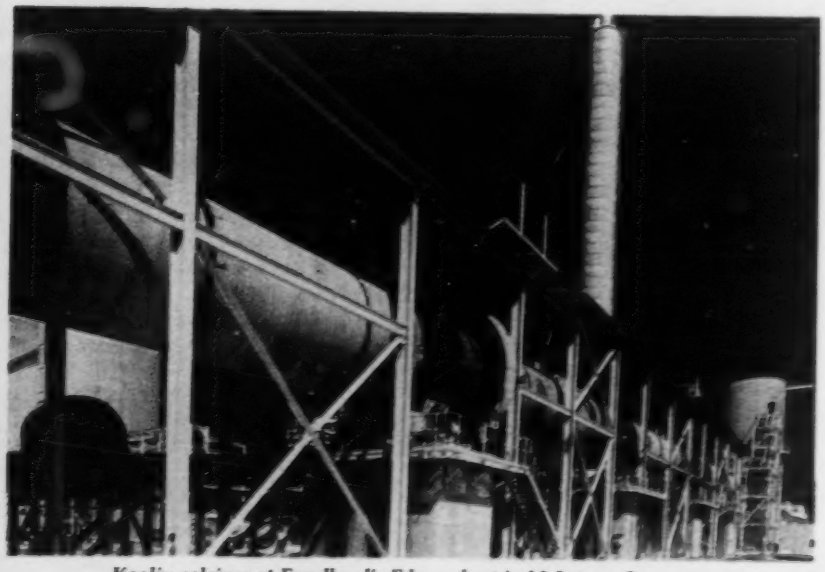
The predominant binder chemistry for coatings is styrene-butadiene latex of which more than 500 million lb is used in the North American paper and paperboard industry, says Frank Cosmi, senior North American marketing manager of Dow Chemical, Midland, Mich.

About 150 million lb of other latexes and polyvinyl acetates are used as binders for coatings. Binder suppliers suggest that there have been moves away from polyvinyl acetate latex and toward styrene-butadiene latex in alkaline environments because polyvinyl acetate latex can cause problems with stickiness on machinery. Natural binders such as starch and protein account for another 750 million lb used in paper and paperboard coatings.

Binders generally are used in combination. Protein is used largely in paperboard, whereas starch and latex are used in higher grade papers. The higher the grade of paper, explains Cosmi, the greater the ratio of synthetic to natural binder. Latexes, which are much more expensive than natural binders, help provide smoothness, gloss, and good printed appearance to coated surfaces. Major latex producers include Dow, GenCorp, BASF, and Rohm & Haas.

Dow sells 80 different latex products for paper coating, based on a wide spectrum of technologies that have developed around the use of different pigments for different types of coated paper. Over the past decade, says Cosmi, growth in coated paper demand and a push toward higher quality papers contributed to a lot of substitution of latex binders for natural binders. The market for latex binders in coatings has had a fairly high growth rate, but now prices are tight. "The forecast is for that growth to taper off a bit," he says. "We are looking more at about 4% annual growth for the remainder of the 1990s.

"There is a public misperception that the paper industry is having to battle and that is that many people believe that coated paper is not necessarily recyclable," says Cosmi. This problem may stem from people being more accustomed to recycling uncoated newspapers and office waste or being aware of functional waterproofing coatings such as waxes or plastics that prevent paper or paperboard from being recycled. "Coated papers, where coatings are applied for printing purposes, are in fact readily recyclable and are recycled today. That's a concern that both the paper industry and the suppliers of binders share."



Kaolin calciner at Engelhard's Edgar plant in McIntyre, Ga.

Alkaline sizing agents benefit

Along with fillers and binders, changes to alkaline papermaking have been a boon to the market for paper-sizing agents. Sizing, which adds the moisture resistance needed for printing, traditionally was based on alum-rosin chemistry in acid papermaking. Alkaline condi-

tions have made it possible for reactive sizes, primarily alkylketene dimer (AKD) and alkyl succinic anhydride (ASA) sizes, to take over the market.

By the end of next year, says Robert Watts, business manager in Cytec's (West Paterson, N.J.) paper chemicals area, 95% of the uncoated free-sheet paper manufacturers in North America will be using alkaline processes. The reactive size market, estimated at about $60 million per year, is shared largely by Cytec, which produces ASA, and Hercules (Wilmington), which produces AKD and is the major producer of rosin-based sizes. Each of the two sizing products offers advantages and disadvantages in certain segments of the paper industry.

With ASA, Cytec focuses on the free-sheet market such as bond paper for forms and offset printing, where the paper is handled through high-speed printers, photocopy machines, or computer printers. Since ASA is very reactive, it typically is emulsified on site with starch (to stabilize and disperse it) and then put into papermaking equipment as an emulsion. The capital investment, about $100,000, is not significant, says Watts, compared with a mill's overall investment in papermaking equipment.

National Starch & Chemical, Bridgewater, N.J., supplies "wet-end" starches that are mixed with the pulp to add strength and retain reactive sizing agents. It also supplies surface starches that are applied after the sheet of paper has been formed to provide surface strength. The market for starches is expected to grow in applications in which starches can help strengthen inherently weaker paper because the paper is lighter weight or it contains more fillers, recycled fibers, or less expensive and weaker groundwood pulp.

A significant amount of starch goes into lightweight, groundwood coated paper, which must be able to withstand repeated runs through printing machines, explains Dennis Boyd, technical manager in National Starch & Chemical's industrial starch division. "Paper that is a better 'runner,' meaning that it runs longer between press cleanups, offers a competitive advantage." In 1989, to meet the need of the market, National Starch & Chemical commercialized a genetically modified corn-based starch called waxy-maize that contains only the high molecular weight, branched amylopectin component of starch.

Despite its need for emulsification, ASA 's faster curing time gives it an advantage over AKD, according to Cytec, and ASA also imparts less slipperiness to the paper—an important feature in cutting and printing applications. "To try to reduce the problems with AKD," says Watts, "some people are putting less internal sizing in the sheet and adding more surface sizes." Therefore, Cytec and other manufacturers are introducing new lines of surface sizes. "It depends on how you want to produce your paper, what is most cost effective, and what gives you the characteristics you want."

In contrast to ASA, however, AKD can be pumped directly into the paper-

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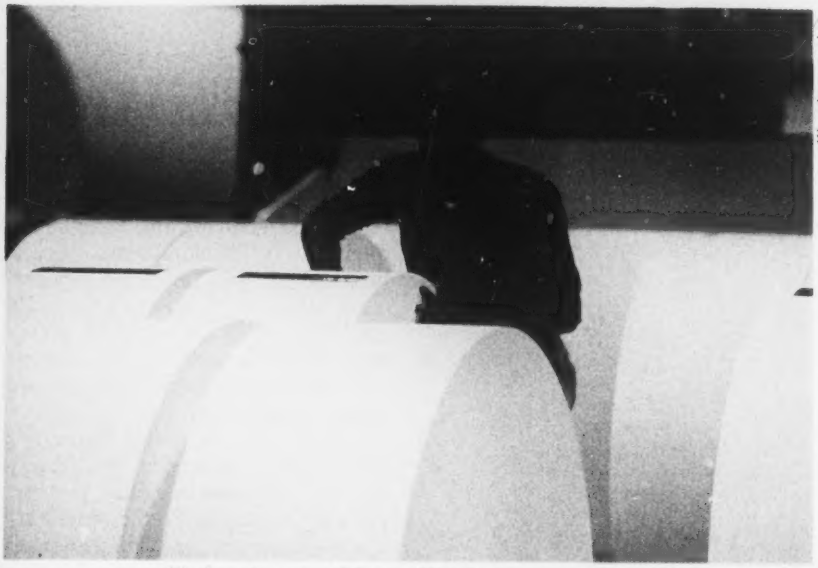

Weyerhaeuser photo

Worker at papermaking facility checks paper strength

making equipment in the same form as it is shipped and can be used in a broad range of applications, including paperboard and cartons. It's also a more powerful sizing agent which makes it applicable for paper-grade with higher filler loadings, says Thomas L. Giles, vice president, Americas, for Hercules' paper technology group. "AKD also runs better on the papermaking equipment, [causing] fewer deposits and [requiring] less cleanup."

Hercules gained its experience in alkaline size technology 20 years ago when Europe started converting from acid to alkaline papermaking, says Giles. Poised for growth today are neutral sizes that will compete with both acid and alkaline sizes. And the recycling of paper is providing challenges to size manufacturers with potentially heavier demands on chemical systems.

Processing aids needed

Heavier demands also may be placed on processing aids used in the production of paper. Processing chemicals include drainage and retention aids, dry-strength resins, wet-strength resins, defoamers, and biocides. Drainage and retention aids are principally specialty polymers, such as polyacrylamides. Dry-strength resins can be starch derivatives, whereas wet-strength resins include polyamides and urea formaldehyde. Hercules, Cytec, Nalco Chemical, Rohm & Haas, Rhône-Poulenc, PPG, and Betz PaperChem are among the suppliers of papermaking processing aids.

When a sheet of paper is formed, a slurry of pulp, fillers, and water is laid out on a screen or mesh. The water is then drained away and squeezed out as the sheets pass through large rollers. Drainage and retention aids allow the water to flow out while the fibers and other materials are retained in the sheet. Thus, the move toward higher filler loadings has increased the demand on retention aids and contributed to growth in that market.

"Today, about one third of the fine paper market uses some type of inorganic microparticle/polyacrylamide-based retention chemistry," says Eric Muchmore, business manager for performance chemicals in Cytec's paper chemicals department. Inorganic microparticles often have limited use because of high costs, variable performance, and handling difficulties. Cytec recently introduced a flexible micropolymer system that can be used with a range of pulps and fillers, he says, and that combines the cost and handling advantages of conventional polymers with the high retention, drainage, and formation benefits of inorganic microparticles.

Polymers are finding increased applications in de-inking processes and recycled papers. Weaker recycled fibers are contributing to growth in drainage and in dry- and wet-strength agents. And in recycling, once inks are separated from paper, polymers and surfactants remove the inks from process waters and effluents.

The removal of inks or toners from paper itself is an area of chemistry under a great deal of development. De-inking chemicals can affect fiber quality as well as the chemistry of later repulping, bleaching, and processing stages. FAS is being considered as a dye stripping and bleaching agent alternative to sodium hypochlorite, which is being phased out because it reduces pulp strength and produces chloroform in effluents.

Wet-strength agents also have been affected by environmental considerations. These materials allow paper products to retain their strength when wet, a useful feature in household products such as paper towels. Many wet-strength agents are based on polyamide epichlorohydrin chemistry, containing chlorinated organic by-products that may appear in paper mill effluents. Giles says that Hercules has introduced products that now have significantly reduced levels of the chlorinated organic by-products.

Bill Drury, assistant vice president for marketing services at Betz PaperChem, Jacksonville, Fla., says all polymer suppliers are having to meet demands for products that simultaneously allow for good drainage, retention, and formation of a sheet of paper. Polymers can provide more uniform formation in paper sheets, preventing breakage during the papermaking process, and improve the printability of the final product.

An individual polymer can enhance both drainage and retention at the same time, he explains, but unfortunately when drainage and retention are increased, formation can decrease. Specialty chemical companies are increasingly turning to multicomponent programs that try to achieve a balance between the three qualities required by paper mills.

Meeting the needs of paper manufacturers has become a continuing challenge not only for specialty, but for all, paper chemical suppliers. Although changes in the papermaking process have led to growth, chemical suppliers still must strike a balance between product performance, environmental considerations, and market demands. The future of the paper industry will depend largely on its improved profitability and the pressures and direction of legislation regarding solid waste, the phasing out of certain chemicals, and other environmental concerns. □